MEMORANDUM

SUBJECT: Revised Methodology and Emission Factors for Estimating Mobile Source PAH Emissions in the National Toxics Inventory

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The purpose of this memorandum is to provide a methodology and emission fractions for estimating exhaust emissions of 16 PAH species to be included in the 1999 NTI.[a] The information provided can also be used to backcast emissions of these compounds in updates to base year inventories as well.

Previous guidance on estimating PAH emission inventories for mobile sources was provided in 1996, and was used to develop the 1996 NTI.[1] This previous guidance is attached (Attachment 1). It provided methods to estimate "sum of 7" and "sum of 16" emissions for PAHs, but not estimates for individual species. In addition, the methods used previously estimated total PAH as a fraction of VOC, and included only PAH found in the particulate.

The revised methodology outlined below is based on more recent data that include gas phase as well as particle phase PAH, and emission factors are given as a function of PM. Inclusion of gas-phase PAHs will substantially increase the mobile source PAH inventory. PAH emissions are expressed as a function of PM because, with the exception of gas-phase PAH from heavy duty diesel engines, there is generally a reasonable correlation between PAH and total carbon emissions.[2] Also, a recent major study expressed particle and gas phase PAH emissions as a fraction of PM mass.[2] Finally, consultation with experts within and external to EPA led to the conclusion that this was a reasonable approach

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[a]Available speciation data do not indicate detectable PAH evaporative emissions from gasoline engines.

given available information. Other studies have also measured PAH emissions.[3, 4,5, 6] The profiles used for on-highway vehicles are from the list of candidate profiles for inclusion in the SPECIATE database, as recommended in a recent Desert Research Institute document prepared for EPA.[7]

This methodology does not include guidance on separating the inventory for gas-phase PAH from the inventory for particle-phase PAH. Separating the gas and particle phase will be necessary for future air quality modeling. This guidance will be provided at a later date.

Highway Mobile Sources

Gasoline Vehicles -- PAH emission factors for light duty gasoline vehicles in milligrams per mile were obtained from data collected as part of recent work done by Norbeck et al. on the FTP, using quartz filters and a PUF/XAD trap.[3] (This work was done for the Coordinating Research Council and the South Coast Air Quality Management District.) There are three other reports, all prepared for CRC, with PAH emissions data.[8, 9, 10] The data in these reports have not yet been reviewed by EPA. The emission factors from the Norbeck et al. work in milligram per mile and as a fraction of total PM10 are presented in Table 1. The gasoline vehicles tested had relatively high particulate matter emission rates. We recommend using the PM fractions for light duty gasoline trucks, heavy duty gasoline vehicles and motorcycles.

Table 1. PAH Emission Factors for Light Duty Gasoline Vehicles (Norbeck et al., 1998, N=20)[b]

PAH	mg/mi	Fraction of PM10
Benzo(a)anthracene	0.008	0.00010
Benzo(a)pyrene	0.008	0.00010
Benzo(b)fluoranthene	0.010	0.00012
Benzo(k)fluoranthene	0.010	0.00012
Chrysene	0.008	0.00010
Dibenz(a,h)anthracene	0.000	0.00000
Indeno(1,2,3-cd)pyrene	0.006	0.00008
Acenaphthene	0.057	0.00073
Acenaphthalene	0.321	0.00412
Anthracene	0.066	0.00085
Benzo(ghi)perylene	0.020	0.00026
Fluoranthene	0.071	0.00091
Fluorene	0.118	0.00151
Napthalene	7.074	0.09073
Phenanthrene	0.198	0.00254
Pyrene	0.097	0.00124

[b]Reference gives single value for benzo(b/k) fluoranthene; values for individual isomers assumed to be half of total.

Light Duty Diesel Vehicles and Trucks – PAH emission factors for light duty diesel vehicles and trucks were obtained from Norbeck et al., 1998. These emission factors are presented in Table 2. Most of the diesel vehicles tested were pre-1986 technology. Emissions of napthalenes and methyl-naphthalenes were relatively lower than for gasoline vehicles tested in the same study.[3]

Table 2. PAH Emission Factors for Light Duty Diesel Vehicles and Trucks (Norbeck et al., 1998, N = 19)[c]

PAH	mg/mi	Fraction of PM10
Benzo(a)anthracene	0.027	0.000048
Benzo(a)pyrene	0.025	0.000045
Benzo(b)fluoranthene	0.044	0.000078
Benzo(k)fluoranthene	0.044	0.000078
Chrysene	0.032	0.000057
Dibenz(a,h)anthracene	0.001	0.000002
Indeno(1,2,3-cd)pyrene	0.012	0.000021
Acenaphthene	0.048	0.000086
Acenaphthalene	0.545	0.000971
Anthracene	0.102	0.000182
Benzo(ghi)perylene	0.030	0.000053
Fluoranthene	0.301	0.000536
Fluorene	0.214	0.000381
Napthalene	2.056	0.003663
Phenanthrene	0.594	0.001058
Pyrene	0.387	0.000689

Heavy Duty Diesel Vehicles – PAH emission factors for heavy duty diesel vehicles were obtained from data collected as part of the Northern Front Range Air Quality Study NFRAQS).[2, 4, 5] These emission factors are presented in Table 3 as a Fraction of PM2.5. Emissions of PAH were determined using groups of vehicles in some cases to obtain sufficient mass for analysis. The 16 vehicles tested in NFRAQS were selected to represent the in-use fleet for the the 1996 calendar year, based on registration data.

[c]Reference gives single value for benzo(b/k) fluoranthene; values for individual isomers assumed to be half of total.

Table 3. PAH Emission Factors for Heavy Duty Diesel Vehicles (NFRAQS)

PAH	Fraction of PM-2.5	Source
Benzo(a)anthracene	0.000040	NFRAQS Report
Benzo(a)pyrene	0.000013	DRI Report (NFRAQS)
Benzo(b)fluoranthene	0.000011	EPA Diesel Report (NFRAQS)
Benzo(k)fluoranthene	0.000011	EPA Diesel Report (NFRAQS)
Chrysene	0.000007	NFRAQS Report
Dibenz(a,h)anthracene	0.000000	DRI Report (NFRAQS)
Indeno(1,2,3-cd)pyrene	0.000001	NFRAQS Report
Acenaphthene	0.000024	DRI Report (NFRAQS)
Acenaphthalene	0.000037	NFRAQS Report
Anthracene	0.000037	DRI Report (NFRAQS)
Benzo(ghi)perylene	0.000009	NFRAQS Report
Fluoranthene	0.000022	DRI Report (NFRAQS)
Fluorene	0.000049	NFRAQS Report
Napthalene	0.001401	DRI Report (NFRAQS)
Phenanthrene	0.000056	DRI Report (NFRAQS)
Pyrene	0.000039	NFRAQS Report

Nonroad Equipment

Diesel Equipment and Distillate Oil Commercial Marine Vessels – PAH fractions of PM for highway heavy duty diesel vehicles obtained from NFRAQS should be used as a surrogate.

Gasoline Equipment – PAH fractions of PM for highway gasoline vehicles should be used a surrogate for 4-stroke engines. For 2-stroke gasoline engines, PAH particulate and vapor phase emissions data are available from two snowmobile engines running on certification gasoline, collected by Southwest Research Institute.[11] One of the engines tested was fan cooled and the other liquid cooled. Composite PAH fractions of PM10 for these engines are given in Table 4. This profile should be used for all nonroad gasoline 2-stroke engines.

Table 4. Nonroad 2-Stroke Engine Emission Fractions of PM10

PAH	Fraction of PM10
Benzo(a)anthracene	0.000034
Benzo(a)pyrene	0.000029
Benzo(b)fluoranthene	0.000016
Benzo(k)fluoranthene	0.000014
Chrysene	0.000021
Dibenz(a,h)anthracene	0.000001
Indeno(1,2,3-cd)pyrene	0.000035
Acenaphthene	0.000002
Acenaphthalene	0.000075
Anthracene	0.000067
Benzo(ghi)perylene	0.000116
Fluoranthene	0.000267
Fluorene	0.000239
Napthalene	0.000004
Phenanthrene	0.000208
Pyrene	0.000318

Locomotives

For locomotives, emission data for particle and gas-phase PAHs from four engines running on three fuels are available from a recent study done at Southwest Research Institute.[12] The three fuels tested were CARB approved on-highway diesel fuel, Federal on-highway fuel, and a high sulfur nonroad fuel. Two of the engines were EMD 2-strokes and two of the engines were GE 4-strokes. The 2-stroke engines represent 70% of the current population. We used the data from the Federal on-highway and nonroad fuels to develop PM fractions for the NTI in every State but California. We also weighted the data for the 2-stroke engines more heavily than the 4-stroke engine data, since more of these engines are currently in-use. PM fractions are given in Table 5. Since locomotives in California use a different fuel than the rest of the country, separate fractions were developed for that State. These fractions are given in Table 6.

Table 5. Locomotive Engine Emission Fractions of PM10 for 49 States

PAH	Fraction of PM10
Benzo(a)anthracene	0.0000166
Benzo(a)pyrene	0.0000027
Benzo(b)fluoranthene	0.0000069
Benzo(k)fluoranthene	0.0000054
Chrysene	0.0000129
Dibenz(a,h)anthracene	0.0000000
Indeno(1,2,3-cd)pyrene	0.0000027
Acenaphthene	0.0000370
Acenaphthalene	0.0004355
Anthracene	0.0001042
Benzo(ghi)perylene	0.0000034
Fluoranthene	0.0000781
Fluorene	0.0001551
Napthalene	0.0025885
Phenanthrene	0.0006106
Pyrene	0.0001136

Table 6 – Locomotive Engine Emission Fractions of PM10 for California

PAH	Fraction of PM10
Benzo(a)anthracene	0.0000127
Benzo(a)pyrene	0.0000044
Benzo(b)fluoranthene	0.0000044
Benzo(k)fluoranthene	0.0000044
Chrysene	0.0000098
Dibenz(a,h)anthracene	0.0000000
Indeno(1,2,3-cd)pyrene	0.0000033
Acenaphthene	0.0000086
Acenaphthalene	0.0002248
Anthracene	0.0000557
Benzo(ghi)perylene	0.0000044
Fluoranthene	0.0000634
Fluorene	0.0000702
Napthalene	0.0018716
Phenanthrene	0.0003044
Pyrene	0.0000827

Aircraft

Commercial -- A study done in 1994 measured particle phase PAH emissions from a CFM-56 Engine Running on JP-5 fuel.[13] No gas phase PAH emission estimates were taken. The data in this study were used to develop PAH/VOC emission fractions for aircraft, which were used in the 1996 NTI.[14, 15] Since this study provided emission estimates in concentrations for different modes of operation, they cannot easily be converted to PAH emission factors per LTO, or some other surrogate for activity. Thus, we recommend continuing to estimate PAH as a function of VOC. PAH/VOC fractions for commercial aircraft are provided in Table 7.

General Aviation Turbine – Data from the study cited above were used with time in mode data more representative of general aviation aircraft.[16] PAH VOC fractions for general aviation turbine engine aircraft are given in Table 7.

General Aviation Piston – PAH/VOC data for non-catalyst light duty gasoline vehicles should be used as a surrogate for general aviation piston engine aircraft. The guidance provided by EPA in 1996 provided a benzo(a)pyrene to HC fraction for these vehicles, as well as ratios of other PAHs to benzo(a)pyrene. These data can be used to estimate fractions for each of the 16 PAH which will be included in the NTI.

Table 7 – PAH/VOC Fractions for Turbine Engine Aircraft

Compound	PAH/VOC -- Commercial Turbine	PAH/VOC -- GA Turbine
Benzo(a)anthracene	6.39E-08	6.10E-08
Benzo(a)pyrene	3.53E-08	3.34E-08
Benzo(b)fluoranthene		
Benzo(k)fluoranthene		
Chrysene	5.72E-08	5.68E-08
Dibenz(a,h)anthracene		
Ideno(1,2,3-cd)pyrene		
Acenaphthene		
Acenaphthylene		
Anthracene	4.05E-07	4.03E-07
Benzo(ghi)perylene	5.88E-09	5.54E-09
Fluoranthene	8.50E-07	8.43E-07
Fluorene		
Naphthalene	4.29E-04	4.30E-04
Phenanthrene	3.79E-06	3.75E-06
Pyrene	1.03E-06	1.03E-06

Attachments

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